



ENVIRONMENTAL PROTECTION AGENCY

40 CFR Parts 50

[EPA-HQ-OAR-2012-0210; FRL-9822-1]

RIN 2060-AP89

**Method for the Determination of Lead in Total Suspended
Particulate Matter**

AGENCY: Environmental Protection Agency (EPA).

ACTION: Final rule.

SUMMARY: The EPA is establishing a new Federal Reference Method (FRM) for measuring Lead (Pb) in total suspended particulate matter (TSP) collected from ambient air. This method is intended for use by analytical laboratories performing the analysis of Pb in TSP to support data collection for the Pb National Ambient Air Quality Standard (NAAQS). The existing FRM for Pb is designated as a new Federal Equivalent Method (FEM), and the currently designated FEMs are retained. This action avoids any disruption to existing Pb monitoring networks and data collection and does not affect the FRM for TSP sample collection (High-Volume Method).

DATES: This final rule is effective on **[INSERT DATE 30 DAYS
AFTER DATE OF PUBLICATION IN THE FEDERAL REGISTER.]**

ADDRESSES: The EPA has established a docket for this action under Docket No. EPA-HQ-OAR-2012-0210. All documents in the docket are listed on the www.regulations.gov website. Although listed in the index, some information is not publicly available, e.g., Confidential Business Information (CBI) or other information whose disclosure is restricted by statute. Certain other material, such as copyrighted material, is not placed on the Internet and will be publicly available only in hard copy form. Publicly available docket materials are available either electronically at www.regulations.gov or in hard copy at the Air Docket, EPA/DC, EPA West, Room 3334, 1301 Constitution Avenue, NW, Washington, DC. The Air Docket and the Public Reading Room are open from 8:30 a.m. to 4:30 p.m., Monday through Friday, excluding legal holidays. The telephone number for the Public Reading Room is (202) 566-1744, and the telephone number for the Air Docket is (202) 566-1742. For additional information about EPA's public docket visit the EPA Docket Center homepage at: <http://www.epa.gov/epahome/dockets.htm>.

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I. Background

A. Purpose of the New Reference Method

On November 12, 2008, the EPA substantially strengthened the NAAQS for Pb (73 FR 66964). The EPA revised the level of the primary (health-based) standard from 1.5 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) of Pb to 0.15 $\mu\text{g}/\text{m}^3$ of Pb measured in TSP and revised the secondary (welfare-based) standard to be identical in all respects to the primary standard. The current Pb in TSP FRM is based on Flame Atomic Absorption Spectroscopy (FAAS) as specified in 40 CFR part 50, Appendix G. The FRM in Appendix G was originally promulgated in 1978 when FAAS was widely used and considered the best available method to support Pb NAAQS data collection at a level of 1.5 $\mu\text{g}/\text{m}^3$. A new Pb in TSP FRM is needed to: 1) take advantage of improved extraction methods that are

now available with improved precision, sample throughput, and extraction efficiency; 2) address advances in measurement technology that have occurred since promulgation of the original FRM; and 3) address the improved measurement sensitivity (detection limits) needed in response to the tightened Pb NAAQS.

The reference method for Pb in TSP includes two parts: the analysis method for Pb in TSP as specified in 40 CFR 50, Appendix G, and the reference method for high-volume sampling of TSP as specified in 40 CFR 50, Appendix B. The new FRM is for the analysis of Pb in TSP based on Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The FRM serves as the definitive method for routinely analyzing Pb for comparison to the NAAQS and also serves as the standard of comparison for determining equivalence of candidate FEMs. This method replaces the existing method in 40 CFR 50, Appendix G. The FRM that was promulgated in 1978 as Appendix G becomes an approved FEM and the currently designated FEMs are retained. The EPA believes this is appropriate because the new FRM is based on two methods that were tested and approved as FEMs (EQL-0510-191 and EQL-0710-192) to ensure comparability with the FAAS method. This approach permits continued use of the legacy FRM (as an FEM) and the existing FEMs. This avoids any disruption to state and local air monitoring agencies using these methods for Pb monitoring. The

reference method for high volume sampling of TSP will continue to be performed in accordance with the FRM described in Appendix B, and, therefore, is not included as part of this FRM.

With the tightened NAAQS in 2008 and the need for increased measurement sensitivity, an improved measurement technology has become available to meet the needs of the current NAAQS. The FAAS method is less frequently used in the Pb ambient monitoring network (about 10 percent of the sites reported Pb in TSP data to the EPA's Air Quality System in 2012 using the FAAS method) and ICP-based methods have increased in popularity. Recently, the FAAS method has mainly been used as the reference method for testing and designation of candidate FEMs for Pb in accordance with 40 CFR 53.33. With the lowered Pb concentration testing range in Part 53 and new requirement for a Method Detection Limit (MDL) of $0.0075 \mu\text{g}/\text{m}^3$ (described below), the FAAS method sensitivity and availability of laboratories with FAAS capability have created some challenges for comparability testing of new FEMs.

In 2008, the EPA also revised the performance-based requirements for Pb FEMs in Part 53. The performance requirements were revised to be consistent with the revised Pb NAAQS level. Specifically, the Pb concentration range at which the FEM comparability testing is conducted was lowered to a

range of 0.045 to 0.375 $\mu\text{g}/\text{m}^3$ and the requirement for a minimum method detection limit was established at 0.0075 $\mu\text{g}/\text{m}^3$. The detection limit of the new FRM is more than adequate to meet the reduced testing range and detection limit requirements. The FRM's average detection limit for Pb-spiked filters is estimated at 0.00009 $\mu\text{g}/\text{m}^3$, which is well below the requirement of 0.0075 $\mu\text{g}/\text{m}^3$.

B. Rationale for Selection of the New Reference Method

The FRM is based on two recently approved FEMs for extracting Pb from glass fiber filters for subsequent analysis by ICP-MS: 1) Method EQL-0510-191 which uses a heated ($80 \pm 5^\circ\text{C}$) ultrasonic water bath with 1.03M nitric (HNO_3)/2.23M hydrochloric (HCl) acids, and 2) Method EQL-0710-192 which uses a heated ($95 \pm 5^\circ\text{C}$) graphite block (hot block) with 3.5 percent volume/volume (v/v) HNO_3 . In selecting this methodology, the EPA's primary considerations were: methods that have already been tested and approved against the FAAS method; use of equipment that is commonly used; a method that is practical (use of a single vessel for the entire extraction process and storage); and a method with improved sensitivity and throughput to increase efficiency and cost effectiveness over the legacy FRM. ICP-MS was chosen as the analytical technique because it

has improved sensitivity, selectivity, linear range, and is more readily available than FAAS in laboratories today.

The FRM uses methods from two existing FEMs that have been proven comparable to FAAS and, therefore, retains consistency with the legacy FRM (Rice, 2013). The FRM is only intended for the analysis of Pb in TSP and allows for the use of glass fiber, quartz, or polytetrafluoroethylene (PTFE) filters. HNO_3 alone is sufficient for the extraction of Pb; however, the ultrasonic extraction method includes HCl to allow monitoring agencies some flexibility for future needs that may include the extraction of other metals. HCl is needed to aid the extraction of other metals that are not easily brought into solution with HNO_3 alone. The FRM was evaluated for the extraction of Pb only. If the FRM is used for metals other than Pb, the user must evaluate the FRM's applicability before use. The hot block extraction method uses only HNO_3 and must also be evaluated by the user before use to extract metals other than Pb.

The approach and key specifications of the method were submitted for peer review to the Clean Air Scientific Advisory Committee (CASAC) Ambient Air Monitoring and Methods Subcommittee. Public meetings were held to discuss the method and related monitoring issues on September 15, 2010. Comments on the method and approach were provided in writing in a letter

dated November 30, 2010 (EPA-CASAC-11-002)¹, forwarded by CASAC to the Administrator.

The CASAC was supportive of the ICP-MS analytical method and found the approach to be appropriate with superior sensitivity and specificity for Pb. The CASAC recommended a strategy, using a performance-based FRM, to provide flexibility for use of non-FRM or FEM measurement methods and recommended that a third extraction method (microwave) be added to the FRM for its greater sample throughput and potential for reduced sample-to-sample variability. The CASAC viewed the comprehensiveness of the FRM test plan to be appropriate, and recommended that the EPA consider separating the extraction methods from the analytical methods so that any of the FRM extraction methods can be used with any of the FRM analytical measurement methods.

The federal reference and equivalence testing method for Pb in 40 CFR 53.33 serves as the performance-based method approach for the FEM approval process. Candidate methods are tested using

¹CASAC's final report on the Approach for the Development of a New Federal Reference Method (FRM) for Lead in Total Suspended Particulates (Pb-TSP) can be found at:
[http://yosemite.epa.gov/sab/sabproduct.nsf/DA39026E54BAF46E8525781D00606633/\\$File/EPA-CASAC-11-002-unsigned.pdf](http://yosemite.epa.gov/sab/sabproduct.nsf/DA39026E54BAF46E8525781D00606633/$File/EPA-CASAC-11-002-unsigned.pdf).

the performance specifications of part 40 CFR part 53 for acceptance and approval as equivalent methods. Users also have the flexibility to test and submit additional extraction and analysis methods for review and approval as equivalent methods. The EPA believes that microwave extraction is a viable option and is already available as an approved FEM². The ultrasonic and hot block approaches are sufficient for the extraction of Pb and provide high sample throughput, low consumable costs, and lower equipment costs while minimizing the risk of cross contamination and sample loss. In addition, the EPA believes that the existing FEMs³ currently provide a wide variety of extraction and analytical methods and the EPA strongly encourages monitoring agencies to consider adopting one of the already approved FEMs in lieu of submitting new FEM applications. The FRM has two extraction methods (heated ultrasonic and hot block) and one analytical method (ICP-MS). The FRM allows for the use of either of the two extraction methods specified with the ICP-MS analytical method. The method also allows for the use of glass

² FEM EQL-0400-0140 (65 FR 26603, May 8, 2000).

³ The list of current FEMs is located at:

<http://epa.gov/ttn/amtic/files/ambient/criteria/reference-equivalent-methods-list.pdf>.

fiber, PTFE, or quartz filter media for the collection of Pb in TSP.

C. Comments on the Proposed Rule

On February 5, 2013, the EPA proposed a new FRM for determination of Pb in TSP (78 FR 8066) and solicited comment on the proposed method. The EPA received one public comment by the close of the public comment period on March 7, 2013. The commenter questioned the meaning of the MDLs estimated from the analysis of blanks. The commenter recommended that an MDL estimated from blanks include the mean of the blanks and be consistent with the Report of the Federal Advisory Committee on Detection and Quantitation (FACDQ) Approaches and Uses in Clean Water Act Programs (FACDQ, 2007). The Federal Advisory Committee recommended that EPA adopt a new procedure for estimated method sensitivity and replace 40 CFR 136, Appendix B (Definition and Procedure for the Determination of the Method Detection Limit) with the new procedure. The FACDQ procedure described an approach for calculating MDLs and quantitation limits. The EPA conducted a pilot study to assess whether the procedure recommended by the FACDQ could generate reliable estimates of the lowest concentration at which measurement quality objectives could be achieved (U.S. EPA, 2011). Based on the pilot study results, the EPA concluded that none of the procedures tested

consistently generated accurate estimates of the lowest concentration at which the study measurement quality objectives were achieved. The EPA believes that more development and testing of the FACDQ procedure are warranted.⁴ Accordingly, based on the currently available information, the EPA believes that the procedures identified in 40 CFR 135, Appendix B are a more appropriate basis for estimating MDLs for the FRM.

The EPA provided estimates in the proposed rule for MDLs based on reagent/filter blanks and reagent/filter blanks spiked with a Pb solution. The EPA estimated MDLs based on 40 CFR 136, Appendix B which recommends that MDLs be determined using a concentration value that is between 1 and 5 times the estimated MDL. However, 40 CFR 136, Appendix B does not specify the use of reagent/filter blanks for estimating the detection limit. The estimate of MDLs based on reagent/filter blanks is not consistent with 40 CFR 136, Appendix B; therefore, the MDL estimates from reagent/filter blanks have been removed. The remaining MDL estimates in Tables 1, 3, and 5 were determined using reagent/filter blanks that were spiked with Pb at three times the estimated detection limit of 0.001 µg/mL. The MDLs were estimated to demonstrate method performance that is more than adequate to meet the MDL requirements of 0.0075 µg/m³ for Pb

⁴ Refer to: <http://water.epa.gov/scitech/methods/cwa/det/index.cfm> for EPA's Procedures for Detection and Quantitation.

in TSP. It is recommended that laboratories performing this method initially estimate MDLs in accordance with 40 CFR 136, Appendix B and confirm the MDLs annually. In addition, the EPA recommends that laboratories consider performing the optional iterative procedure in part 136, Appendix B to verify the reasonableness of the initially estimated MDL and subsequent MDL determinations.

D. Conclusions

After consideration of the public comment on the estimate of MDL from reagent/filter blanks, the EPA has concluded that the rule should be consistent with the provisions of 40 CFR 136, Appendix B. Accordingly, any language referring to the estimate of MDLs using reagent/filter blanks and the MDLs estimated from reagent/filter blanks in Tables 1, 3, and 5 have been removed. The MDLs estimated from the Pb-spiked reagent/filter blanks remain and demonstrate that the method has more than adequate sensitivity to support the Pb-TSP MDL requirement of 0.0075 $\mu\text{g}/\text{m}^3$. No other comments were received nor revisions made to the proposed rule. The rule is otherwise finalized as proposed.

II. Summary of Method

The FRM uses the ambient air sample collection procedures of the high-volume TSP method (40 CFR part 50, Appendix B) and the analytical procedure for the measurement of Pb based on ICP-

MS. Two extraction methods are used: one using heated ultrasonic and one using hot block digestion. The extraction methods and ICP-MS analysis method have been tested and found acceptable for extraction of Pb from glass fiber, PTFE, or quartz filter media. This method also met the precision and bias goals for Pb in TSP (Rice 2013). This method replaces the previous FRM specified in 40 CFR 50, Appendix G. Although the previous FRM in Appendix G is adequate, this method offers advantages over the previous FRM by providing improved sensitivity or detection limits, precision, sample throughput, and extraction efficiency.

III. Statutory and Executive Order Reviews

A. Executive Order 12866: Regulatory Planning and Review and Executive Order 13563: Improving Regulation and Regulatory Review

This action is not a "significant regulatory action" under the terms of Executive Order 12866 (58 FR 51735, October 4, 1993) and is, therefore, not subject to review under Executive Orders 12866 and 13563 (76 FR 3821, January 21, 2011).

B. Paperwork Reduction Act

This action does not impose an information collection burden under the provisions of the Paperwork Reduction Act, 44 U.S.C. 3501 et seq. Burden is defined at 5 CFR 1320.3(b). This

rule is to promulgate a new FRM for Pb in TSP, and to designate the existing FRM as an FEM, and does not add any information collection requirements beyond those imposed by the existing Pb monitoring requirements.

C. Regulatory Flexibility Act

The Regulatory Flexibility Act (RFA) generally requires an agency to prepare a regulatory flexibility analysis of any rule subject to notice and comment rulemaking requirements under the Administrative Procedure Act or any other statute unless the agency certifies that the rule will not have a significant economic impact on a substantial number of small entities. Small entities include small businesses, small organizations, and small governmental jurisdictions.

For purposes of assessing the impacts of this rule on small entities, small entity is defined as (1) a small business as defined by the Small Business Administration's (SBA) regulations at 13 CFR 121.201; (2) a small governmental jurisdiction that is a government of a city, county, town, school district or special district with a population of less than 50,000; and (3) a small organization that is any not-for-profit enterprise which is independently owned and operated and is not dominant in its field.

After considering the economic impacts of this rule on small entities, I certify that this action will not have a significant economic impact on a substantial number of small entities. This rule will not impose any additional monitoring requirements beyond those specified in the current regulations, nor will it require any changes in approved monitoring methods. As such, it will not impose any requirements on small entities.

D. Unfunded Mandates Reform Act

This action contains no federal mandates under the provisions of Title II of the Unfunded Mandates Reform Act of 1995 (UMRA), 2 U.S.C. 1531-1538 for state, local, or tribal governments or the private sector. This action imposes no enforceable duty on any state, local or tribal governments or the private sector. Therefore, this action is not subject to the requirements of sections 202 or 205 of the UMRA. This action is also not subject to the requirements of section 203 of UMRA because it contains no regulatory requirements that might significantly or uniquely affect small governments. This action establishes a new FRM for state and local air monitoring agencies to use as one of the approved methods for measurement of Pb in TSP and to designate the existing FRM as an FEM. It does not create any additional monitoring requirements or require changes in approved monitoring methods.

E. Executive Order 13132: Federalism

This action does not have federalism implications. It will not have substantial direct effects on the states, on the relationship between the national government and the states, or on the distribution of power and responsibilities among the various levels of government, as specified in Executive Order 13132. This action establishes a new FRM for state and local air monitoring agencies to use as one of the approved methods for measurement of Pb in TSP and designates the existing FRM as an FEM. This action does not create any new monitoring requirements or require any changes in approved monitoring methods. Thus, Executive Order 13132 does not apply to this action.

F. Executive Order 13175: Consultation and Coordination with Indian Tribal Governments

This action does not have tribal implications, as specified in Executive Order 13175 (65 FR 67249, November 9, 2000). This rule imposes no requirements on tribal governments. This action establishes a new FRM for state and local air monitoring agencies to use as one of the approved methods for measurement of Pb in TSP and designates the existing FRM as an FEM. This action does not create any new monitoring requirements, nor require any changes in approved monitoring methods. Thus, Executive Order 13175 does not apply to this action.

G. Executive Order 13045: Protection of Children from Environmental Health and Safety Risks

The EPA interprets EO 13045 (62 F.R. 19885, April 23, 1997) as applying only to those regulatory actions that concern health or safety risks, such that the analysis required under section 5-501 of the EO has the potential to influence the regulation. This action is not subject to EO 13045 because it does not establish an environmental standard intended to mitigate health or safety risks.

H. Executive Order 13211: Actions Concerning Regulations That Significantly Affect Energy Supply, Distribution, or Use

This action is not subject to Executive Order 13211 (66 FR 28355 (May 22, 2001)), because it is not a significant regulatory action under Executive Order 12866.

I. National Technology Transfer and Advancement Act

Section 12(d) of the National Technology Transfer and Advancement Act of 1995 ("NTTAA"), Public Law No. 104-113 (15 U.S.C. 272 note), directs the EPA to use voluntary consensus standards in its regulatory activities unless to do so would be inconsistent with applicable law or otherwise impractical. Voluntary consensus standards are technical standards (e.g., materials specifications, test methods, sampling procedures, and business practices) that are developed or adopted by voluntary

consensus standards bodies. NTTAA directs the EPA to provide Congress, through OMB, explanations when the agency decides not to use available and applicable voluntary consensus standards.

This rule involves environmental monitoring and measurement consistent with the agency's Performance Based Measurement System (PBMS). The PBMS approach is intended to be more flexible and cost-effective for the regulated community; it is also intended to encourage innovation in analytical technology and improved data quality. Specifically, this rule establishes a new FRM for Pb in TSP measurements. The EPA used voluntary consensus standards in the preparation of this FRM. The FRM is the benchmark against which all ambient monitoring methods are compared. The FRM is not a voluntary consensus standard.

The FEM equivalency criteria contained in 40 CFR 53 constitute performance criteria. Therefore, the EPA is not precluding the use of any method, whether it constitutes a voluntary consensus standard or not, as long as it meets the specified performance criteria in 40 CFR 53 and is approved by the EPA pursuant to those regulations.

J. Executive Order 12898: Federal Actions to Address Environmental Justice in Minority Populations and Low-Income Populations

Executive Order (EO) 12898 (59 FR 7629 (Feb. 16, 1994)) establishes federal executive policy on environmental justice. Its main provision directs federal agencies, to the greatest extent practicable and permitted by law, to make environmental justice part of their mission by identifying and addressing, as appropriate, disproportionately high and adverse human health or environmental effects of their programs, policies, and activities on minority populations and low-income populations in the United States.

The EPA has determined that this rule will not have disproportionately high and adverse human health or environmental effects on minority or low-income populations because it does not affect the level of protection provided to human health or the environment. This action establishes a new FRM for state and local air monitoring agencies to use as one of the approved methods for measurement of Pb in TSP and designates the existing FRM as an FEM.

K. Congressional Review Act

The Congressional Review Act, 5 U.S.C. 801 et seq., as added by the Small Business Regulatory Enforcement Fairness Act of 1996, generally provides that before a rule may take effect, the agency promulgating the rule must submit a rule report, which includes a copy of the rule, to each House of the Congress

and to the Comptroller General of the United States. The EPA will submit a report containing this rule and other required information to the U.S. Senate, the U.S. House of Representatives, and the Comptroller General of the United States prior to publication of the rule in the Federal Register. A major rule cannot take effect until 60 days after it is published in the Federal Register. This action is not a "major rule" as defined by 5 U.S.C. 804(2). This rule will be effective **[INSERT DATE 30 DAYS AFTER DATE OF PUBLICATION IN THE FEDERAL REGISTER.]**

List of Subjects in 40 CFR Part 50

Environmental protection, Air pollution control, and Lead.

Dated: June 26, 2013

Bob Perciasepe,
Acting Administrator.

For reasons stated in the preamble, title 40, chapter I of the Code of Federal Regulations sets forth the following.

PART 50—NATIONAL PRIMARY AND SECONDARY AMBIENT AIR QUALITY STANDARDS

1. The authority citation for part 50 continues to read as follows:

Authority: 42 U.S.C. 7401, et seq.

2. Appendix G to part 50 is revised to read as follows:

Appendix G to Part 50 - Reference Method for the Determination of Lead in Total Suspended Particulate Matter

1.0 Scope and applicability

Based on review of the air quality criteria and national ambient air quality standard (NAAQS) for lead (Pb) completed in 2008, the EPA made revisions to the primary and secondary NAAQS for Pb to protect public health and welfare. The EPA revised the level from 1.5 $\mu\text{g}/\text{m}^3$ to 0.15 $\mu\text{g}/\text{m}^3$ while retaining the current indicator of Pb in total suspended particulate matter (Pb-TSP).

Pb-TSP is collected for 24 hours on a TSP filter as described in Appendix B of part 50, the Reference Method for the Determination of Suspended Particulate Matter in the Atmosphere (High-Volume Method). This method is for the analysis of Pb from

TSP filters by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using a heated ultrasonic bath with nitric acid (HNO_3) and hydrochloric acid (HCl) or a heated block (hot block) digester with HNO_3 for filter extraction.

This method is based on the EPA's Office of Solid Waste (SW-846) Method 6020A - Inductively Coupled Plasma Mass Spectrometry (U.S. EPA, 2007). Wording in certain sections of this method is paraphrased or taken directly from Method 6020A.

1.1 ICP-MS is applicable for the sub- $\mu\text{g}/\text{mL}$ (ppb) determination of Pb in a wide variety of matrices. Results reported for monitoring or compliance purposes are calculated in $\mu\text{g}/\text{m}^3$ at local conditions (LC). This procedure describes a method for the acid extraction of Pb in particulate matter collected on glass fiber, quartz, or PTFE filters and measurement of the extracted Pb using ICP-MS.

1.2 Due to variations in the isotopic abundance of Pb, the value for total Pb must be based on the sum of the signal intensities for isotopic masses, 206, 207, and 208. Most instrument software packages are able to sum the primary isotope signal intensities automatically.

1.3 ICP-MS requires the use of an internal standard. ^{115}In (Indium), ^{165}Ho (Holmium), and ^{209}Bi (Bismuth) are recommended internal standards for the determination of Pb.

1.4 Use of this method is restricted to use by, or under supervision of, properly trained and experienced laboratory personnel. Requirements include training and experience in inorganic sample preparation, including acid extraction, and also knowledge in the recognition and in the correction of spectral, chemical and physical interference in ICP-MS.

2.0 Summary of method

2.1 This method describes the acid extraction of Pb in particulate matter collected on glass fiber, quartz, or PTFE ambient air filters with subsequent measurement of Pb by ICP-MS. Estimates of the Method Detection Limit (MDL) or sensitivity of the method are provided in Tables 1, 3 and 5 and determined using Pb-spiked filters or filter strips analyzed in accordance with the guidance provided in 40 CFR 136, Appendix B - Determination and procedures for the Determination of the Method Detection Limit - Revision 1.1. The analytical range of the method is $0.00024 \mu\text{g}/\text{m}^3$ to $0.60 \mu\text{g}/\text{m}^3$, and based on the low and high calibration curve standards and a nominal filter sample volume of 2000 m^3 .

2.2 This method includes two extraction methods. In the first method, a solution of HNO_3 and HCl is added to the filters or filter strips in plastic digestion tubes and the tubes are placed in a heated ultrasonic bath for one hour to facilitate

the extraction of Pb. Following ultrasonication, the samples are brought to a final volume of 40 mL (50 mL for PTFE filters), vortex mixed or shaken vigorously, and centrifuged prior to aliquots being taken for ICP-MS analysis. In the second method, a solution of dilute HNO_3 is added to the filter strips in plastic digestion tubes and the tubes placed into the hot block digester. The filter strip is completely covered by the solution. The tubes are covered with polypropylene watch glasses and refluxed. After reflux, the samples are diluted to a final volume of 50 mL with reagent water and mixed before analysis.

2.3 Calibration standards and check standards are prepared to matrix match the acid composition of the samples. ICP-MS analysis is then performed. With this method, the samples are first aspirated and the aerosol thus created is transported by a flow of argon gas into the plasma torch. The ions produced (e.g., Pb^{+1}) in the plasma are extracted via a differentially-pumped vacuum interface and are separated on the basis of their mass-to-charge ratio. The ions are quantified by a channel electron multiplier or a Faraday detector and the signal collected is processed by the instrument's software. Interferences must be assessed and corrected for, if present.

3.0 Definitions

Pb - Elemental or ionic lead

HNO₃ - Nitric acid

HCl - Hydrochloric acid

ICP-MS - Inductively Coupled Plasma Mass Spectrometer

MDL - Method detection limit

RSD - Relative standard deviation

RPD - Relative percent difference

CB - Calibration Blank

CAL - Calibration Standard

ICB - Initial calibration blank

CCB - Continuing calibration blank

ICV - Initial calibration verification

CCV - Continuing calibration verification

LLCV - Lower Level Calibration Verification, serves as
the lower level ICV and lower level CCV

RB - Reagent blank

RBS - Reagent blank spike

MSDS - Material Safety Data Sheet

NIST - National Institute of Standards and Technology

D.I. water - Deionized water

SRM - NIST Standard Reference Material

CRM - Certified Reference Material

EPA - Environmental Protection Agency

v/v - volume to volume ratio

4.0 Interferences

4.1 Reagents, glassware, plasticware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. If reagent blanks, filter blanks, or quality control blanks yield results above the detection limit, the source of contamination must be identified. All containers and reagents used in the processing of the samples must be checked for contamination prior to sample extraction and analysis. Reagents shall be diluted to match the final concentration of the extracts and analyzed for Pb. Labware shall be rinsed with dilute acid solution and the solution analyzed. Once a reagent or labware article (such as extraction tubes) from a manufacturer has been successfully screened, additional screening is not required unless contamination is suspected.

4.2 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z) as the species of interest. There are no species found in ambient air that will result in isobaric interference with the three Pb isotopes (206, 207, and 208) being measured. Polyatomic interferences occur when two or more elements combine to form an ion with the same mass-to-charge ratio as the isotope being measured. Pb is not

subject to interference from common polyatomic ions and no correction is required.

4.3 The distribution of Pb isotopes is not constant. The analysis of total Pb should be based on the summation of signal intensities for the isotopic masses 206, 207, and 208. In most cases, the instrument software can perform the summation automatically.

4.4 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers of the ICP-MS. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement. These interferences are compensated for by use of internal standards. Sample dilution will reduce the effects of high levels of dissolved salts, but calibration standards must be prepared in the extraction medium and diluted accordingly.

4.5 Memory interferences are related to sample transport and result when there is carryover from one sample to the next. Sample carryover can result from sample deposition on the sample and skimmer cones and from incomplete rinsing of the sample

solution from the plasma torch and the spray chamber between samples. These memory effects are dependent upon both the analyte being measured and sample matrix and can be minimized through the use of suitable rinse times.

5.0 Health and safety cautions

5.1 The toxicity or carcinogenicity of reagents used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Each laboratory is responsible for maintaining a current file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in the chemical analysis. Specifically, concentrated HNO_3 presents various hazards and is moderately toxic and extremely irritating to skin and mucus membranes. Use this reagent in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing, and observe proper mixing when working with these reagents.

5.2 Concentrated HNO_3 and HCl are moderately toxic and extremely irritating to the skin. Use these reagents in a fume

hood, and if eye and skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection when working with these reagents. The component of this procedure requiring the greatest care is HNO_3 . HNO_3 is a strong, corrosive, oxidizing agent that requires protection of the eyes, skin, and clothing. Items to be worn during use of this reagent include:

1. Safety goggles (or safety glasses with side shields),
2. Acid resistant rubber gloves, and
3. A protective garment such as a laboratory apron. HNO_3 spilled on clothing will destroy the fabric; contact with the skin underneath will result in a burn.

It is also essential that an eye wash fountain or eye wash bottle be available during performance of this method. An eye wash bottle has a spout that covers the eye. If acid or any other corrosive gets into the eye, the water in this bottle is squirted onto the eye to wash out the harmful material. Eye washing should be performed with large amounts of water immediately after exposure. Medical help should be sought immediately after washing. If either acid, but especially HNO_3 , is spilled onto the skin, wash immediately with large amounts of water. Medical attention is not required unless the burn appears to be significant. Even after washing and drying, HNO_3 may leave

the skin slightly brown in color; this will heal and fade with time.

5.3 Pb salts and Pb solutions are toxic. Great care must be taken to ensure that samples and standards are handled properly; wash hands thoroughly after handling.

5.4 Care must be taken when using the ultrasonic bath and hot block digester as they are capable of causing mild burns. Users should refer to the safety guidance provided by the manufacturer of their specific equipment.

5.5 Analytical plasma sources emit radio frequency radiation in addition to intense ultra violet (UV) radiation. Suitable precautions should be taken to protect personnel from such hazards. The inductively coupled plasma should only be viewed with proper eye protection from UV emissions.

6.0 Equipment

6.1 Thermo Scientific X-Series ICP-MS or equivalent. The system must be capable of providing resolution better or equal to 1.0 atomic mass unit (amu) at 10 percent peak height. The system must have a mass range from at least 7 to 240 amu that allows for the application of the internal standard technique. For the measurement of Pb, an instrument with a collision or reaction cell is not required.

6.2 Ultrasonic extraction equipment

6.2.1 Heated ultrasonic bath capable of maintaining a temperature of 80°C; VWR Model 750HT, 240W, or equivalent.

Ultrasonic bath must meet the following performance criteria:

1. Cut a strip of aluminum foil almost the width of the tank and double the depth.

2. Turn the ultrasonic bath on and lower the foil into the bath vertically until almost touching the bottom of the tank and hold for 10 seconds.

3. Remove the foil from the tank and observe the distribution of perforations and small pin prick holes. The indentations should be fine and evenly distributed. The even distribution of indentations indicates the ultrasonic bath is acceptable for use.

6.2.2 Laboratory centrifuge, Beckman GS-6, or equivalent.

6.2.3 Vortex mixer, VWR Signature Digital Vortex Mixer, VWR Catalog No. 14005-824, or equivalent.

6.3 Hot block extraction equipment

6.3.1 Hot block digester, SCP Science DigiPrep Model MS, No. 010-500-205 block digester capable of maintaining a temperature of 95°C, or equivalent.

6.4 Materials and Supplies

- Argon gas supply, 99.99 percent purity or better.
National Welders Microbulk, or equivalent.
- Plastic digestion tubes with threaded caps for extraction and storage, SCP Science DigiTUBE® Item No. 010-500-063, or equivalent.
- Disposable polypropylene ribbed watch glasses (for heated block extraction), SCP Science Item No. 010-500-081, or equivalent.
- Pipette, Rainin EDP2, 100 μ L, \pm 1 percent accuracy, \leq 1 percent RSD (precision), with disposable tips, or equivalent.
- Pipette, Rainin EDP2, 1000 μ L, \pm 1 percent accuracy, \leq 1 percent RSD (precision), with disposable tips, or equivalent.
- Pipette, Rainin EDP2, 1-10 mL, \pm 1 percent accuracy, \leq 1 percent RSD (precision), with disposable tips, or equivalent.
- Pipette, Thermo Lab Systems, 5 mL, \pm 1 percent accuracy, \leq 1 percent RSD (precision), with disposable tips, or equivalent.
- Plastic tweezer, VWR Catalog No. 89026-420, or equivalent.
- Laboratory marker.

- Ceramic knife, Kyocera LK-25, and non-metal ruler or other suitable cutting tools for making straight cuts for accurately measured strips.
- Blank labels or labeling tape, VWR Catalog No. 36425-045, or equivalent.
- Graduated cylinder, 1 L, VWR 89000-260, or equivalent.
- Volumetric flask, Class A, 1 L, VWR Catalog No. 89025-778, or equivalent.
- Millipore Element deionized water system, or equivalent, capable of generating water with a resistivity of $\geq 17.9 \text{ M}\Omega\text{-cm}$).
- Disposable syringes, 10-mL, with 0.45 micron filters (must be Pb-free).
- Plastic or PTFE wash bottles.
- Glassware, Class A - volumetric flasks, pipettes, and graduated cylinders.
- Glass fiber, quartz, or PTFE filters from the same filter manufacturer and lot used for sample collection for use in the determination of the MDL and for laboratory blanks.

7.0 Reagents and standards

7.1 Reagent - or trace metals-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

7.2 Concentrated nitric acid, 67-70 percent, SCP Science Catalog No. 250-037-177, or equivalent.

7.3 Concentrated hydrochloric acid (for the ultrasonic extraction method), 33-36 percent, SCP Science Catalog No. 250-037-175, or equivalent.

7.4 Deionized water - All references to deionized water in the method refer to deionized water with a resistivity $\geq 17.9 \text{ M}\Omega\text{-cm}$.

7.5 Standard stock solutions may be commercially purchased for each element or as a multi-element mix. Internal standards may be purchased as a mixed multi-element solution. The manufacturer's expiration date and storage conditions must be adhered to.

7.5.1 Lead standard, 1000 $\mu\text{g/mL}$, NIST traceable, commercially available with certificate of analysis. High Purity Standards Catalog No. 100028-1, or equivalent.

7.5.2 Indium (In) standard, 1000 µg/mL, NIST traceable, commercially available with certificate of analysis. High Purity Standards Catalog No. 100024-1, or equivalent.

7.5.3 Bismuth (Bi) standard, 1000 µg/mL, NIST traceable, commercially available with certificate of analysis. High Purity Standards Catalog No. 100006-1, or equivalent.

7.5.4 Holmium (Ho) standard, 1000 µg/mL, NIST traceable, commercially available with certificate of analysis. High Purity Standards Catalog No. 100023-1, or equivalent.

7.5.5 Second source lead standard, 1000 µg/mL, NIST traceable, commercially available with certificate of analysis. Must be from a different vendor or lot than the standard described in 7.5.1. Inorganic Ventures Catalog No. CGPB-1, or equivalent.

7.5.6 Standard Reference Materials, NIST SRM 2583, 2586, 2587 or 1648, or equivalent.⁵

Note: The In, Bi, and Ho internal standards may also be purchased as 10 µg/mL standards. Calibration standards are prepared by diluting stock standards to the appropriate levels in the same acid concentrations as in the final sample volume. The typical range for calibration standards is 0.001 to 2.00

⁵ Certificates of Analysis for these SRMs can be found at:

<http://www.nist.gov/srm/index.cfm>

µg/mL. At a minimum, the curve must contain a blank and five Pb containing calibration standards. The calibration standards are stored at ambient laboratory temperature. Calibration standards must be prepared weekly and verified against a freshly prepared ICV using a NIST-traceable source different from the calibration standards.

7.6 Internal standards may be added to the test solution or by on-line addition. The nominal concentration for an internal standard is 0.010 µg/mL (10 ppb). Bismuth (Bi) or holmium (Ho) are the preferred internal standards for Pb, but indium (In) may be used in the event the sample contains Bi and high recoveries are observed.

7.7 Three laboratory blank solutions are required for analysis: (1) the calibration blank is used in the construction of the calibration curve and as a periodic check of system cleanliness (ICB and CCB); (2) the reagent blank (RB) is carried through the extraction process to assess possible contamination; and (3) the rinse blank is run between samples to clean the sample introduction system. If RBs or laboratory blanks yield results above the detection limit, the source of contamination must be identified. Screening of labware and reagents is addressed in Section 4.1.

7.7.1 The calibration blank is prepared in the same acid matrix as the calibration standards and samples and contains all internal standards used in the analysis.

7.7.2 The RB contains all reagents used in the extraction and is carried through the extraction procedure at the same time as the samples.

7.7.3 The rinse blank is a solution of 1 to 2 percent HNO_3 (v/v) in reagent grade water. A sufficient volume should be prepared to flush the system between all standards and samples analyzed.

7.7.4 The EPA currently provides glass fiber, quartz, and PTFE filters to air monitoring agencies as requested annually. As part of the procurement process, these filters are tested for acceptance by the EPA. The current acceptance criteria for glass fiber and quartz filters is 15 μg per filter or 0.0075 $\mu\text{g}/\text{m}^3$ using a nominal sample volume of 2000 m^3 and 4.8 ng/cm^2 or 0.0024 $\mu\text{g}/\text{m}^3$ for PTFE filters using a nominal sample volume of 24 m^3 . Acceptance test results for filters obtained by the EPA are typically well below the criterion specified and also below the recently revised Pb method performance detection limit of 0.0075 $\mu\text{g}/\text{m}^3$; therefore, blank subtraction should not be performed.

7.7.5 If filters are not provided by the EPA for sample collection and analysis, filter lot blanks should be analyzed

for Pb content. For large filter lots (>500 filters), randomly select 20 to 30 filters from the lot and analyze the filter or filter strips for Pb. For smaller filter lots, a lesser number of filters can be analyzed. Glass, quartz and PTFE filters must not have levels of Pb above the criteria specified in section 7.7.4 and, therefore, blank correction should not be performed. If acceptance testing shows levels of Pb above the criteria in Section 7.7.4, corrective action must be taken to reduce the levels before proceeding.

7.8 The Initial Calibration Verification (ICV), Lower Level Calibration Verification (LLCV), and Continuing Calibration Verification (CCV) solutions are prepared from a different Pb source than the calibration curve standards and at a concentration that is either at or below the midpoint on the calibration curve, but within the calibration range. Both are prepared in the same acid matrix as the calibration standards. Note that the same solution may be used for both the ICV and CCV. The ICV/CCV and LLCV solutions must be prepared fresh daily.

7.9 Tuning Solution. Prepare a tuning solution according to the instrument manufacturer's recommendations. This solution will be used to verify the mass calibration and resolution of the instrument.

8.0 Quality Control (QC)

8.1 Standard QC practices shall be employed to assess the validity of the data generated, including: MDL, RB, duplicate samples, spiked samples, serial dilutions, ICV, CCV, LLCV, ICB, CCB, and SRMs/CRMs.

8.2 MDLs must be calculated in accordance with 40 CFR part 136, Appendix B. RBs with low-level standard spikes are used to estimate the MDL. The low-level standard spike is added to at least 7 individual filter strips and then carried through the entire extraction procedure. This will result in at least 7 individual samples to be used for the MDL. The recommended range for spiking the strips is 1 to 5 times the estimated MDL.

8.3 For each batch of samples, one RB and one reagent blank spike (RBS) that is spiked at the same level as the sample spike (see Section 8.6) must be prepared and carried throughout the entire process. The results of the RB must be below 0.001 µg/mL. The recovery for the RBS must be within ± 20 percent of the expected value. If the RB yields a result above 0.001 µg/mL, the source of contamination must be identified and the extraction and analysis repeated. Reagents and labware must be suspected as sources of contamination. Screening of reagents and labware is addressed in Section 4.1.

8.4 Any samples that exceed the highest calibration standard must be diluted and rerun so that the concentration falls within the curve. The minimum dilution will be 1 to 5 with matrix matched acid solution.

8.5 The internal standard response must be monitored during the analysis. If the internal standard response falls below 70 percent or rises above 120 percent of expected due to possible matrix effects, the sample must be diluted and reanalyzed. The minimum dilution will be 1 to 5 with matrix matched acid solution. If the first dilution does not correct the problem, additional dilutions must be run until the internal standard falls within the specified range.

8.6 For every batch of samples prepared, there must be one duplicate and one spike sample prepared. The spike added is to be at a level that falls within the calibration curve, normally the midpoint of the curve. The initial plus duplicate sample must yield a relative percent difference ≤ 20 percent. The spike must be within ± 20 percent of the expected value.

8.7 For each batch of samples, one extract must be diluted five-fold and analyzed. The corrected dilution result must be within ± 10 percent of the undiluted result. The sample chosen for the serial dilution shall have a concentration at or above 10X the lowest standard in the curve to ensure the diluted value

falls within the curve. If the serial dilution fails, chemical or physical interference should be suspected.

8.8 ICB, ICV, LLCV, CCB and CCV samples are to be run as shown in the following table.

Sample	Frequency	Performance Specification
ICB	Prior to first sample	Less than 0.001 $\mu\text{g/mL}$
ICV	Prior to first sample	Within 90 to 110 percent of the expected value
LLCV	Daily, before first sample and after last sample	± 10 percent of the expected value
CCB	After every 10 extracted samples	Less than 0.001 $\mu\text{g/mL}$
CCV	After every 10 extracted samples	Within 90-110 percent of the expected value

If any of these QC samples fails to meet specifications, the source of the unacceptable performance must be determined,

the problem corrected, and any samples not bracketed by passing QC samples must be reanalyzed.

8.9 For each batch of samples, one certified reference material (CRM) must be combined with a blank filter strip and carried through the entire extraction procedure. The result must be within ± 10 percent of the expected value.

8.10 For each run, a LLCV must be analyzed. The LLCV must be prepared at a concentration not more than three times the lowest calibration standard and at a concentration not used in the calibration curve. The LLCV is used to assess performance at the low end of the curve. If the LLCV fails (± 10 percent of the expected value) the run must be terminated, the problem corrected, the instrument recalibrated, and the analysis repeated.

8.11 Pipettes used for volumetric transfer must have the calibration checked at least once every 6 months and pass ± 1 percent accuracy and ≤ 1 percent RSD (precision) based on five replicate readings. The pipettes must be checked weekly for accuracy with a single replicate. Any pipette that does not meet ± 1 percent accuracy on the weekly check must be removed from service, repaired, and pass a full calibration check before use.

8.12 Samples with physical deformities are not quantitatively analyzable. The analyst should visually check

filters prior to proceeding with preparation for holes, tears, or non-uniform deposit which would prevent representative sampling. Document any deformities and qualify the data with flags appropriately. Care must be taken to protect filters from contamination. Filters must be kept covered prior to sample preparation.

9.0 ICP-MS Calibration

Follow the instrument manufacturer's instructions for the routine maintenance, cleaning, and ignition procedures for the specific ICP-MS instrument being used.

9.1 Ignite the plasma and wait for at least one half hour for the instrument to warm up before beginning any pre-analysis steps.

9.2 For the Thermo X-Series with Xt cones, aspirate a 10 ng/mL tuning solution containing In, Bi, and Ce (Cerium). Monitor the intensities of In, Bi, Ce, and CeO (Cerium oxide) and adjust the instrument settings to achieve the highest In and Bi counts while minimizing the CeO/Ce oxide ratio. For other instruments, follow the manufacturer's recommended practice. Tune to meet the instrument manufacturer's specifications. After tuning, place the sample aspiration probe into a 2 percent HNO₃ rinse solution for at least 5 minutes to flush the system.

9.3 Aspirate a 5 ng/mL solution containing Co, In, and Bi to perform a daily instrument stability check. Run 10 replicates of the solution. The percent RSD for the replicates must be less than 3 percent at all masses. If the percent RSD is greater than 3 percent, the sample introduction system, pump tubing, and tune should be examined, and the analysis repeated. Place the sample aspiration probe into a 2 percent HNO₃ rinse solution for at least 5 minutes to flush the system.

9.4 Load the calibration standards in the autosampler and analyze using the same method parameters that will be used to analyze samples. The curve must include one blank and at least 5 Pb-containing calibration standards. The correlation coefficient must be at least 0.998 for the curve to be accepted. The lowest standard must recover ± 15 percent of the expected value and the remaining standards must recover ± 10 percent of the expected value to be accepted.

9.5 Immediately after the calibration curve is completed, analyze an ICV and an ICB. The ICV must be prepared from a different source of Pb than the calibration standards. The ICV must recover 90-110 percent of the expected value for the run to continue. The ICB must be less than 0.001 $\mu\text{g/mL}$. If either the ICV or the ICB fails, the run must be terminated, the problem identified and corrected, and the analysis re-started.

9.6 A LLCV, CCV and a CCB must be run after the ICV and ICB. A CCV and CCB must be run at a frequency of not less than every 10 extracted samples. A typical analytical run sequence would be: Calibration blank, Calibration standards, ICV, ICB, LLCV, CCV, CCB, Extracts 1-10, CCV, CCB, Extracts 11-20, CCV, CCB, Extracts 21-30, CCV, CCB, LLCV, CCV, CCB. Extracts are any field sample or QC samples that have been carried through the extraction process. The CCV solution is prepared from a different source than the calibration standards and may be the same as the ICV solution. The LLCV must be within ± 10 percent of expected value. The CCV value must be within ± 10 percent of expected for the run to continue. The CCB must be less than 0.001 $\mu\text{g/mL}$. If either the CCV, LLCV, or CCB fails, the run must be terminated, the problem identified and corrected, and the analysis re-started from the last passing CCV/LLCV/CCB set.

9.7 A LLCV, CCV, and CCB set must be run at the end of the analysis. The LLCV must be within ± 30 percent of expected value. If either the CCV, LLCV, or CCB fails, the run must be terminated, the problem identified and corrected, and the analysis re-started from the last passing CCV/LLCV/CCB set.

10.0 Heated Ultrasonic Filter Strip Extraction

All plasticware (e.g., Nalgene) and glassware used in the extraction procedures is soaked in 1 percent HNO_3 (v/v) for at

least 24 hours and rinsed with reagent water prior to use. All mechanical pipettes used must be calibrated to ± 1 percent accuracy and ≤ 1 percent RSD at a minimum of once every 6 months.

10.1 Sample Preparation - Heated Ultrasonic Bath

10.1.1 Extraction solution (1.03M HNO₃ + 2.23M HCl).

Prepare by adding 500 mL of deionized water to a 1000 mL flask, adding 64.4 mL of concentrated HNO₃ and 182 mL of concentrated HCl, shaking to mix, allowing solution to cool, diluting to volume with reagent water, and inverting several times to mix. Extraction solution must be prepared at least weekly.

10.1.2 Use a ceramic knife and non-metal ruler, or other cutting device that will not contaminate the filter with Pb. Cut a 3/4 inch X 8 inch strip from the glass fiber or quartz filter by cutting a strip from the edge of the filter where it has been folded along the 10 inch side at least 1 inch from the right or left side to avoid the un-sampled area covered by the filter holder. The filters must be carefully handled to avoid dislodging deposits.

10.1.3 Using plastic tweezers, roll the filter strip up in a coil and place the rolled strip in the bottom of a labeled 50 mL extraction tube. In a fume hood, add 15.00 ± 0.15 mL of the extraction solution (see Section 10.1.1) using a calibrated

mechanical pipette. Ensure that the extraction solution completely covers the filter strip.

10.1.4 Loosely cap the 50 mL extraction tube and place it upright in a plastic rack. When all samples have been prepared, place the racks in an uncovered heated ultrasonic water bath that has been preheated to $80 \pm 5^{\circ}\text{C}$ and ensure that the water level in the ultrasonic is above the level of the extraction solution in the tubes but well below the level of the extraction tube caps to avoid contamination. Start the ultrasonic bath and allow the unit to run for 1 hour \pm 5 minutes at $80 \pm 5^{\circ}\text{C}$.

10.1.5 Remove the rack(s) from the ultrasonic bath and allow the racks to cool.

10.1.6 Add 25.00 ± 0.25 mL of D.I. water with a calibrated mechanical pipette to bring the sample to a final volume of 40.0 ± 0.4 mL. Tightly cap the tubes, and vortex mix or shake vigorously. Place the extraction tubes in an appropriate holder and centrifuge for 20 minutes at 2500 revolutions per minute (RPM) .

CAUTION - Make sure that the centrifuge holder has a flat bottom to support the flat bottomed extraction tubes.

10.1.7 Pour an aliquot of the solution into an autosampler vial for ICP-MS analysis to avoid the potential for

contamination. Do not pipette an aliquot of solution into the autosampler vial.

10.1.8 Decant the extract to a clean tube, cap tightly, and store the sample extract at ambient laboratory temperature. Extracts may be stored for up to 6 months from the date of extraction.

10.2 47 mm PTFE Filter Extraction - Heated Ultrasonic Bath

10.2.1 Extraction solution (1.03M HNO₃ + 2.23M HCl).

Prepare by adding 500 mL of D.I. water to a 1000mL flask, adding 64.4 mL of concentrated HNO₃ and 182 mL of concentrated HCl, shaking to mix, allowing solution to cool, diluting to volume with reagent water, and inverting several times to mix. Extraction solution must be prepared at least weekly.

10.2.2 Using plastic tweezers, bend the PTFE filter into a U-shape and insert the filter into a labeled 50 mL extraction tube with the particle loaded side facing the center of the tube. Gently push the filter to the bottom of the extraction tube. In a fume hood, add 25.00 ± 0.15 mL of the extraction solution (see Section 10.2.1) using a calibrated mechanical pipette. Ensure that the extraction solution completely covers the filter.

10.2.3 Loosely cap the 50 mL extraction tube and place it upright in a plastic rack. When all samples have been prepared,

place the racks in an uncovered heated ultrasonic water bath that has been preheated to $80 \pm 5^{\circ}\text{C}$ and ensure that the water level in the ultrasonic is above the level of the extraction solution in the tubes, but well below the level of the extraction tube caps to avoid contamination. Start the ultrasonic bath and allow the unit to run for 1 hour \pm 5 minutes at $80 \pm 5^{\circ}\text{C}$.

10.2.4 Remove the rack(s) from the ultrasonic bath and allow the racks to cool.

10.2.5 Add 25.00 ± 0.25 mL of D.I. water with a calibrated mechanical pipette to bring the sample to a final volume of 50.0 ± 0.4 mL. Tightly cap the tubes, and vortex mix or shake vigorously. Allow samples to stand for one hour to allow complete diffusion of the extracted Pb. The sample is now ready for analysis.

NOTE: Although PTFE filters have only been extracted using the ultrasonic extraction procedure in the development of this FRM, PTFE filters are inert and have very low Pb content. No issues are expected with the extraction of PTFE filters using the heated block digestion method. However, prior to using PTFE filters in the heated block extraction method, extraction method performance test using CRMs must be done to confirm performance (see Section 8.9).

11.0 Hot Block Filter Strip Extraction

All plasticware (e.g., Nalgene) and glassware used in the extraction procedures is soaked in 1 percent HNO_3 for at least 24 hours and rinsed with reagent water prior to use. All mechanical pipettes used must be calibrated to ± 1 percent accuracy and ≤ 1 percent RSD at a minimum of once every 6 months.

11.1 Sample Preparation - Hot Block Digestion

11.1.1 Extraction solution (1:19, v/v HNO_3). Prepare by adding 500 mL of D.I. water to a 1000 mL flask, adding 50 mL of concentrated HNO_3 , shaking to mix, allowing solution to cool, diluting to volume with reagent water, and inverting several times to mix. The extraction solution must be prepared at least weekly.

11.1.2 Use a ceramic knife and non-metal ruler, or other cutting device that will not contaminate the filter with Pb. Cut a 1-inch X 8-inch strip from the glass fiber or quartz filter. Cut a strip from the edge of the filter where it has been folded along the 10-inch side at least 1 inch from the right or left side to avoid the un-sampled area covered by the filter holder. The filters must be carefully handled to avoid dislodging particle deposits.

11.1.3 Using plastic tweezers, roll the filter strip up in a coil and place the rolled strip in the bottom of a labeled 50

mL extraction tube. In a fume hood, add 20.0 ± 0.15 mL of the extraction solution (see Section 11.1.1) using a calibrated mechanical pipette. Ensure that the extraction solution completely covers the filter strip.

11.1.4 Place the extraction tube in the heated block digester and cover with a disposable polyethylene ribbed watch glass. Heat at $95 \pm 5^{\circ}\text{C}$ for 1 hour and ensure that the sample does not evaporate to dryness. For proper heating, adjust the temperature control of the hot block such that an uncovered vessel containing 50 mL of water placed in the center of the hot block can be maintained at a temperature approximately, but no higher than 85°C . Once the vessel is covered with a ribbed watch glass, the temperature of the water will increase to approximately 95°C .

11.1.5 Remove the rack(s) from the heated block digester and allow the samples to cool.

11.1.6 Bring the samples to a final volume of 50 mL with D.I. water. Tightly cap the tubes, and vortex mix or shake vigorously for at least 5 seconds. Set aside (with the filter strip in the tube) for at least 30 minutes to allow the HNO_3 trapped in the filter to diffuse into the extraction solution.

11.1.7 Shake thoroughly (with the filter strip in the digestion tube) and let settle for at least one hour. The sample is now ready for analysis.

12.0 Measurement Procedure

12.1 Follow the instrument manufacturer's startup procedures for the ICP-MS.

12.2 Set instrument parameters to the appropriate operating conditions as presented in the instrument manufacturer's operating manual and allow the instrument to warm up for at least 30 minutes.

12.3 Calibrate the instrument per Section 9.0 of this method.

12.4 Verify the instrument is suitable for analysis as defined in Sections 9.2 and 9.3.

12.5 As directed in Section 8.0 of this method, analyze an ICV and ICB immediately after the calibration curve followed by a LLCV, then CCV and CCB. The acceptance requirements for these parameters are presented in Section 8.8.

12.6 Analyze a CCV and a CCB after every 10 extracted samples.

12.7 Analyze a LLCV, CCV and CCB at the end of the analysis.

12.8 A typical sample run will include field samples, field sample duplicates, spiked field sample extracts, serially diluted samples, the set of QC samples listed in Section 8.8 above, and one or more CRMs or SRMs.

12.9 Any samples that exceed the highest standard in the calibration curve must be diluted and reanalyzed so that the diluted concentration falls within the calibration curve.

13.0 Results

13.1 The filter results must be initially reported in $\mu\text{g/mL}$ as analyzed. Any additional dilutions must be accounted for. The internal standard recoveries must be included in the result calculation; this is done by the ICP-MS software for most commercially-available instruments. Final results should be reported in $\mu\text{g Pb/m}^3$ to three significant figures as follows:

$$C = ((\mu\text{g Pb/mL} * V_f * A) * D) / V_s$$

Where:

C = Concentration, $\mu\text{g Pb/m}^3$

$\mu\text{g Pb/mL}$ = Lead concentration in solution

V_f = Total extraction solution volume

A = Area correction; $\frac{3}{4}$ " X 8" strip = 5.25 in² analyzed, A = 12.0 or 1" X 8" strip = 7 in² analyzed, A = 9.0

D = dilution factor (if required)

V_s = Actual volume of air sampled

The calculation assumes the use of a standard 8-inch X 10-inch TSP filter which has a sampled area of 9-inch X 7-inch (63.0 in^2) due to the $\frac{1}{2}$ -inch filter holder border around the outer edge. The $\frac{3}{4}$ -inch X 8-inch strip has a sampled area of $\frac{3}{4}$ -inch X 7-inch (5.25 in^2). The 1-inch X 8-inch strip has a sampled area of 1-inch X 7-inch (7.0 in^2). If filter lot blanks are provided for analysis, refer to Section 7.7.5 of this method for guidance on testing.

14.0 Method Performance

Information in this section is an example of typical performance results achieved by this method. Actual performance must be demonstrated by each individual laboratory and instrument.

14.1 Performance data have been collected to estimate MDLs for this method. MDLs were determined in accordance with 40 CFR 136, Appendix B. MDLs were estimated for glass fiber, quartz, and PTFE filters using seven reagent/filter blank solutions spiked with low level Pb at three times the estimated MDL of $0.001 \text{ } \mu\text{g/mL}$. Tables 1, 3, and 5 shows the MDLs estimated using both the ultrasonic and hot block extraction methods for glass fiber and quartz filters and the ultrasonic method for PTFE filters. The MDLs are well below the EPA requirement of five percent of the current Pb NAAQS or $0.0075 \text{ } \mu\text{g/m}^3$. These MDLs are

provided to demonstrate the adequacy of the method's performance for Pb in TSP. Each laboratory using this method should determine MDLs in their laboratory and verify them annually. It is recommended that laboratories also perform the optional iterative procedure in 40 CFR 136, Appendix B to verify the reasonableness of the estimated MDL and subsequent MDL determinations.

14.2 Extraction method recovery tests with glass fiber and quartz filter strips, and PTFE filters spiked with NIST SRMs were performed using the ultrasonic/HNO₃ and HCl filter extraction methods and measurement of the dissolved Pb with ICP-MS. Tables 2, 4, and 6 show recoveries obtained with these SRM. The recoveries for all SRMs were ≥ 90 percent at the 95 percent confidence level.

Table 1: Method Detection Limits Determined by Analysis of Reagent/Glass Fiber Filter Blanks Spiked with Low-level Pb Solution.

	Ultrasonic Extraction	Hotblock Extraction
	Method	Method
	$\mu\text{g}/\text{m}^3$ *	$\mu\text{g}/\text{m}^3$ *
n=1	0.0000702	0.000533
n=2	0.0000715	0.000482
n=3	0.0000611	0.000509

n=4	0.0000587	0.000427
n=5	0.0000608	0.000449
n=6	0.0000607	0.000539
n=7	0.0000616	0.000481
Average	0.0000635	0.000489
Standard Deviation	0.0000051	0.000042
MDL**	0.0000161	0.000131

* Assumes 2000 m³ of air sampled.

** MDL is 3.143 times the standard deviation of the results for seven sample replicates analyzed.

Table 2: Recoveries of Lead from NIST SRMs Spiked onto Glass Fiber Filters.

Extraction Method	Recovery, ICP-MS, (percent)			
	NIST 1547 Plant	NIST 2709 Soil	NIST 2583 Dust	NIST 2582 Paint
Ultrasonic Bath	100±4	98±1	103±8	101±0
Block Digestion	92±7	98±3	103±4	94±4

Table 3: Method Detection Limits Determined by Analysis of Reagent/Quartz Filter Blanks Spiked with Low-level Pb Solution.

	Ultrasonic Extraction	Hotblock Extraction
	Method $\mu\text{g}/\text{m}^3$ *	Method $\mu\text{g}/\text{m}^3$ *
n=1	0.000533	0.000274
n=2	0.000552	0.000271
n=3	0.000534	0.000281
n=4	0.000684	0.000269
n=5	0.000532	0.000278
n=6	0.000532	0.000272
n=7	0.000552	0.000261
Average	0.000560	0.000272
Standard Deviation	0.000055	0.000007
MDL**	0.000174	0.000021

* Assumes 2000 m³ of air sampled.

** MDL is 3.143 times the standard deviation of the results for seven sample replicates analyzed.

Table 4: Recoveries of Lead from NIST SRMs Spiked onto Quartz Fiber Filters.

Extraction	
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Method	Recovery, ICP-MS, (percent)			
	NIST 1547 Plant	NIST 2709 Soil	NIST 2583 Dust	NIST 2582 Paint
Ultrasonic Bath	101±6	95±1	91±5	93±1
Block Digestion	106±3	104±3	92±6	95±2

Table 5: Method Detection Limits Determined by Analysis of Reagent/PTFE Filter Blanks Spiked with Low-level Pb Solution.

	Ultrasonic Extraction Method
	$\mu\text{g}/\text{m}^3$ *
n=1	0.001775
n=2	0.001812
n=3	0.001773
n=4	0.001792
n=5	0.001712
n=6	0.001767
n=7	0.001778
Average	0.001773
Standard	0.000031
MDL**	0.000097

* Assumes 24 m³ of air sampled.

** MDL is 3.143 times the standard deviation of the results for seven sample replicates analyzed.

Table 6: Recoveries of Lead from NIST SRMs Spiked onto PTFE Filters.

Extraction Method	Recovery, ICP-MS, (percent)			
	NIST 1547	NIST 2709	NIST 2583	NIST 2582
	Plant	Soil	Dust	Paint
Ultrasonic Bath	104±5	93±1	108±11	96±3

15.0 Pollution Prevention

15.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. The sources of pollution generated with this procedure are waste acid extracts and Pb-containing solutions.

15.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult

Less is Better: Laboratory Chemical Management for Waste Reduction, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St. N.W., Washington, D.C., 20036, www.acs.org.

16.0 Waste Management

16.1 Laboratory waste management practices must be conducted consistent with all applicable rules and regulations. Laboratories are urged to protect air, water, and land by minimizing all releases from hood and bench operations, complying with the letter and spirit of any sewer and discharge permits and regulations, and by complying with all solid and hazardous waste regulation. For further information on waste management, consult The Waste Management Manual for Laboratory Personnel available from the American Chemical Society listed in Section 15.2 of this method.

16.2 Waste HNO_3 , HCl , and solutions containing these reagents and/or Pb must be placed in labeled bottles and delivered to a commercial firm that specializes in removal of hazardous waste.

17.0 References

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